

LA-UR -80-460

MASTER

TITLE: UNITARY BASES FOR X-RAY PHOTOELECTRON SPECTROSCOPY

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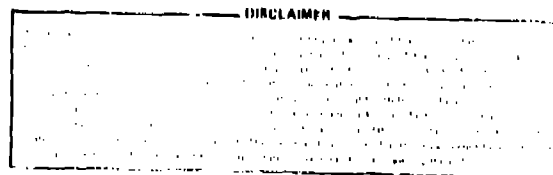
Presented at the Unitary Group Conference
Bielefeld, Germany.

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UNITARY BASES FOR X-RAY PHOTOELECTRON SPECTROSCOPY

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Abstract

A Gelfand basis is used to derive the coefficients of fractional parentage (CFP's) used to calculate intensities for x-ray photoelectron spectroscopy of atoms. Using associated Gelfand bases, we show that it is easy to derive the Racah CFP relations between "particles" and "holes."

The use of unitary techniques to calculate electronic matrix elements for atomic configurations has the advantage of avoiding the use of coefficients of fractional parentage (CFP's), sums over permutations, and recoupling coefficients.¹⁻¹⁰ However, in order to relate the unitary approach to that of Racah,¹¹ we wish to show the ease in which CFP's can be derived using a unitary basis. Furthermore, we show that Racah's relationships between CFP's for "particles" and "holes" follow naturally using the unitary approach.

The mathematical problem treated here is equivalent to the derivation of the relative number of electrons which will be found in the lowest energy peaks of an x-ray photoelectron spectrum of an atom. Assume the atom has an outer shell configuration of n different ℓ -electrons and before irradiation is known to be in a state $|\ell^n \bar{M}_L, S\rangle$ with total orbital angular momentum L and spin S . The probability that the atom will be left in a state $|\ell^{n-1} \bar{M}_L, \bar{S}\rangle$ after irradiation is simply

$$T = \frac{N}{[L]} \sum_{\bar{M}_L, \bar{M}_L} |\langle \ell^{n-1} \bar{M}_L, \bar{S} | x | \ell^n \bar{M}_L, S \rangle|^2, \quad [L] = 2L+1, \quad (1)$$

where we sum over final states \bar{M}_L and average over initial states M_L . We shall derive the normalization constant N below. The unitary generator

$$E_{xq} = \sum_{i=1}^n a_x^{\dagger} a_q^{\dagger} \quad (2)$$

is a multipole operator which destroys any particle in state $|\ell q^{-1}\rangle$ and creates a scattered state $|x^{\dagger}\rangle$.

The description of the emission state $|x\rangle$ is left rather vague. Since no polarization or angular dependence is included, we shall assume that $|x\rangle$ is a spherically symmetric s -state $|\ell=0, m=0\rangle$. That is

$$E_{xq} = (-1)^q V_{-q}^{\ell} = (-1)^q \sum_{i=1}^n v_{-q}^{\ell}(i) \quad (3)$$

such that

$${}^n\langle 00 | E_{xq} | \ell q \rangle^n = {}^n\langle 00 | (-1)^q V_{-q}^{\ell}(n) | \ell q \rangle^n = 1 \quad , \quad (4)$$

if the n th particle is in state $|\ell q\rangle$. Clearly, a more detailed picture which accounts for polarized x-rays and the target structure will give rise to more complicated tensorial forms than in Eq. (3).

From the definition of CFP's below for antisymmetrized spin-orbit states

$$\begin{aligned} \langle \Lambda_{n-1} \ell^{n-1} \bar{L}_L, \bar{S}_S; x | (-1)^q V_{-q}^{\ell} | \Lambda_n \ell^n L_L, S_S \rangle \\ = \sqrt{n} C_{M_S, M_L}^{\bar{S}, S} C_{M_L, M_L}^{\bar{L}, \ell} (\ell^{n-1} \bar{L}_S |) \ell^n L_S \rangle \quad , \end{aligned} \quad (5)$$

it follows that

$$\begin{aligned} | \langle \ell^{n-1} \bar{L}_L, \bar{S}; x | E_{xq} | \ell^n L_L, S \rangle |^2 \\ = n \left(C_{M_L, q}^{\bar{L}, \ell} C_{M_L, M_L}^{\bar{L}, \ell} \right)^2 (\ell^{n-1} \bar{L}_S |) \ell^n L_S \rangle^2 \quad . \end{aligned} \quad (6)$$

The above equation is a consequence of the fact that

$$\begin{aligned} \langle \Lambda_{n-1} \ell^{n-1} \bar{L}_L, \bar{S}_S; x | E_{xq} | \Lambda_n \ell^n L_L, S_S \rangle \\ = C_{M_S, M_S}^{\bar{S}, S} \langle \ell^{n-1} \bar{L}_L, \bar{S}; x | E_{xq} | \ell^n L_L, S \rangle \end{aligned} \quad (7)$$

as shown by Drake and Schlesinger.¹²

From Eq. (1) we find

$$T = (\ell^{n-1} \bar{L}_S |) \ell^n L_S \rangle \quad (8)$$

where

$$N = \frac{\ell}{n} \quad .$$

The total probability is then

$$\sum_{\bar{L}\bar{S}} (e^{n-L-\bar{L}} | e^n_{L\bar{S}}) = 1$$

as desired. The fact that the photoelectron spectral intensities are proportional to the CFP's was originally shown by Cox and Orchard.¹³

We can now evaluate the CFP's in Eq. (6) using Gelfand bases. We first need to expand the states $|e^n M_L, S\rangle$ in terms of Gelfand states. This has been done by Caird¹⁴ for all shells up to $\ell = 3$ (f-electrons) and is effected by lowering from the highest M_L state ($M_L = L$) which is always a simple Gelfand state.^{3,6}

For example, below are some states for the n -shell up to the half-filled n^3 configuration

$$\begin{aligned} |p^1 P1, \frac{1}{2}\rangle &= \boxed{1} \\ |p^1 P0, \frac{1}{2}\rangle &= \boxed{2} \\ |p^1 P-1, \frac{1}{2}\rangle &= \boxed{3} \end{aligned} \quad (9)$$

$$\begin{aligned} |p^2 P1, 1\rangle &= \boxed{\frac{1}{2}} \\ |p^2 P0, 1\rangle &= \boxed{\frac{1}{3}} \\ |p^2 P-1, 1\rangle &= \boxed{\frac{2}{3}} \\ |p^2 D2, 0\rangle &= \boxed{\frac{1}{1}} \\ |p^2 D1, 0\rangle &= \boxed{\frac{1}{2}} \\ |p^2 D0, 0\rangle &= \sqrt{\frac{1}{3}} \boxed{\frac{1}{3}} + \sqrt{\frac{2}{3}} \boxed{22} \\ |p^2 D-1, 0\rangle &= \boxed{\frac{2}{3}} \\ |p^2 D-2, 0\rangle &= \boxed{\frac{3}{3}} \end{aligned} \quad (10)$$

$$\begin{aligned} |p^3 D2, \frac{1}{2}\rangle &= \boxed{\frac{1}{2}} \\ |p^3 D1, \frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} \boxed{\frac{1}{2}} + \sqrt{\frac{1}{2}} \boxed{\frac{1}{3}} \\ |p^3 D0, \frac{1}{2}\rangle &= \sqrt{\frac{3}{4}} \boxed{\frac{1}{3}} + \sqrt{\frac{1}{4}} \boxed{\frac{1}{2}} \\ |p^3 D-1, \frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} \boxed{\frac{1}{3}} + \sqrt{\frac{1}{2}} \boxed{\frac{2}{3}} \\ |p^3 D-2, \frac{1}{2}\rangle &= \boxed{\frac{2}{3}} \end{aligned}$$

$$\begin{aligned} |p^3 P1, \frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} \boxed{\frac{1}{2}} - \sqrt{\frac{1}{2}} \boxed{\frac{1}{3}} \\ |p^3 P0, \frac{1}{2}\rangle &= -\sqrt{\frac{1}{4}} \boxed{\frac{1}{3}} + \sqrt{\frac{3}{4}} \boxed{\frac{1}{2}} \\ |p^3 P-1, \frac{1}{2}\rangle &= \sqrt{\frac{1}{2}} \boxed{\frac{1}{3}} - \sqrt{\frac{1}{2}} \boxed{\frac{2}{3}} \end{aligned} \quad (11)$$

Now if we order the states as in Eq. (9) such that the $q = \ell, \ell-1, \dots, -\ell; x$ are $1, 2, \dots, 2\ell+1; 2\ell+2$ then E_{xq} is an elementary generator of $SU(2\ell+2)$ for $q = -\ell$. The matrix elements of the elementary generators may be readily evaluated in the Gelfand basis using the algorithms shown in Fig. 1.^{4,6} We note that the phases in Fig. 1 differ from those used by Drake and Schlesinger in Ref. 12 to derive Eq. (7). However, since we are concerned with the absolute value of the CFP's, Eq. (6) is still valid.

From Fig. 1 we find, using $q = -\ell$

(a) $\langle T' | E_{ii} | T \rangle = \delta_{T',T} \left(\begin{array}{c} \text{number} \\ \text{of } (i)'s \end{array} \right)$

(b) $\langle T' | E_{ij} | T \rangle = \langle T | E_{ji} | T' \rangle$

(c) $\langle \begin{array}{|c|} \hline i-1 \\ \hline i-1 \\ \hline \end{array} | E_{i-1,i} | \begin{array}{|c|} \hline i \\ \hline i-1 \\ \hline \end{array} \rangle = \sqrt{\frac{d+1}{d}} = \langle \begin{array}{|c|} \hline i \\ \hline i-1 \\ \hline \end{array} | E_{i-1,i} | \begin{array}{|c|} \hline i-1 \\ \hline i \\ \hline \end{array} \rangle$

(d) $\langle \begin{array}{|c|} \hline i-1 \\ \hline i \\ \hline \end{array} | E_{i-1,i} | \begin{array}{|c|} \hline i \\ \hline i \\ \hline \end{array} \rangle = \sqrt{\frac{d-1}{d}} = \langle \begin{array}{|c|} \hline i-1 \\ \hline i-1 \\ \hline \end{array} | E_{i-1,i} | \begin{array}{|c|} \hline i-1 \\ \hline i \\ \hline \end{array} \rangle$

(e) $E_{23} \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 3 & 3 \\ \hline \end{array} = \frac{1}{\sqrt{2}} \begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & 3 \\ \hline \end{array} + \frac{1}{\sqrt{2}} \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 2 & 3 \\ \hline \end{array}$

(f) $E_{12} \begin{array}{|c|c|} \hline 1 & 2 \\ \hline 1 & 1 \\ \hline \end{array} = \sqrt{2} \begin{array}{|c|c|} \hline 1 & 1 \\ \hline 1 & 1 \\ \hline \end{array}$

(g) $\langle \begin{array}{|c|} \hline i-1 \\ \hline \end{array} | E_{i-1,i} | \begin{array}{|c|} \hline i \\ \hline \end{array} \rangle = 1 = \langle \begin{array}{|c|} \hline i-1 \\ \hline \end{array} | E_{i-1,i} | \begin{array}{|c|} \hline i-1 \\ \hline \end{array} \rangle$

(h) $\langle \begin{array}{|c|} \hline i-1 \\ \hline i-1 \\ \hline \end{array} | E_{i-1,i} | \begin{array}{|c|} \hline i \\ \hline i \\ \hline \end{array} \rangle = 1 = \langle \begin{array}{|c|} \hline i-1 \\ \hline i-1 \\ \hline \end{array} | E_{i-1,i} | \begin{array}{|c|} \hline i-1 \\ \hline i-1 \\ \hline \end{array} \rangle$

Fig.1. Tableau Formulas for Electronic Orbital Operators

(a) Number operators E_{ii} are diagonal. (The only eigenvalues for orbital states are 0, 1, and 2.)

(b) Raising and lowering operators are simply transposes of each other.

(c-h) $E_{i-1,i}$ acting on a tableau state gives zero unless there is an (i) in a column of the tableau that doesn't already have an (i-1), too. Then it gives back a new state with the (i) changed to (i-1) and a factor (matrix element) that depends on where the other (i)'s and (i-1)'s are located.

(Boxes not outlined in the figure contain numbers not equal to (i) or (i-1).) Cases (c) and (d) involved the "city block" distance d

which is the denominator of the matrix element. The numerator is one larger ($d+1$) or smaller ($d-1$) depending on whether the involved tableaux favor the larger or smaller state number (i or i-1) with a higher position.

The special cases of ($d=1$) shown in (f) always pick the larger (and non-zero) choice of $d+1=2$. All other non-zero matrix elements are equal to unity.

$$\begin{aligned}
E_{xq} |p^3 \text{ } P-1, \frac{1}{2}\rangle &= E_{43} \left(\sqrt{\frac{1}{2}} \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 3 & \\ \hline \end{array} - \sqrt{\frac{1}{2}} \begin{array}{|c|c|} \hline 2 & 2 \\ \hline 3 & \\ \hline \end{array} \right) \\
&= \sqrt{\frac{1}{2}} \left(\sqrt{\frac{3}{2}} \begin{array}{|c|c|} \hline 1 & 4 \\ \hline 3 & \\ \hline \end{array} + \sqrt{\frac{1}{2}} \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 4 & \\ \hline \end{array} \right) - \sqrt{\frac{1}{2}} \begin{array}{|c|c|} \hline 2 & 2 \\ \hline 4 & \\ \hline \end{array} \\
&= \left(\sqrt{\frac{3}{4}} \begin{array}{|c|} \hline 1 \\ \hline 3 \\ \hline \end{array} + \sqrt{\frac{1}{4}} \begin{array}{|c|c|} \hline 1 & 3 \\ \hline \end{array} - \sqrt{\frac{1}{2}} \begin{array}{|c|c|} \hline 2 & 2 \\ \hline \end{array} \right) \cdot \begin{array}{|c|} \hline 4 \\ \hline \end{array} \\
&= \sqrt{\frac{3}{4}} |p^2 \text{ } P0,1;x\rangle - \sqrt{\frac{1}{12}} |p^2 \text{ } D0,0;x\rangle \\
&\quad + \sqrt{\frac{2}{3}} |p^2 \text{ } S0,0;x\rangle
\end{aligned} \tag{12}$$

From Eq. 6 we find

$$\begin{aligned}
\frac{3}{4} &= 3(C_{0-1-1}^{1 \ 1 \ 1})^2 (p^2 \text{ } P1|) p^3 P_{\frac{1}{2}})^2 \\
\frac{1}{12} &= 3(C_{0-1-1}^{2 \ 1 \ 1})^2 (p^2 \text{ } D0|) p^3 P_{\frac{1}{2}})^2 \\
\frac{2}{3} &= 3(C_{0-1-1}^{0 \ 1 \ 1})^2 (p^2 \text{ } S0|) p^3 P_{\frac{1}{2}})^2
\end{aligned} \tag{13}$$

Evaluating the Clebsch-Gordon coefficients, we have the following three relative photoelectron intensities:

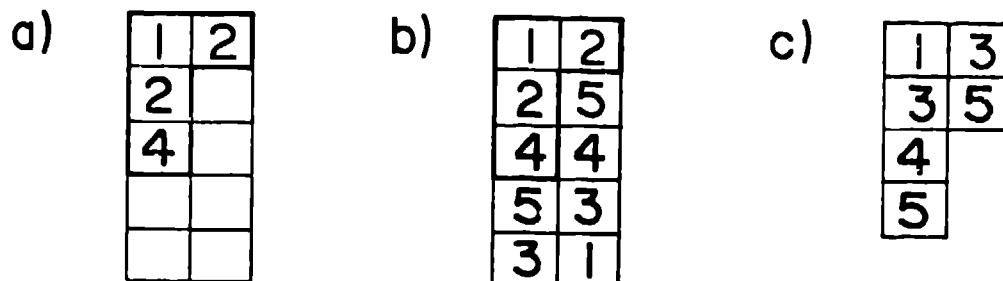
$$\begin{aligned}
(p^2 \text{ } P1|) p^3 P_{\frac{1}{2}})^2 &= 1/2 \\
(p^2 \text{ } D0|) p^3 P_{\frac{1}{2}})^2 &= 5/18 \\
(p^2 \text{ } S0|) p^3 P_{\frac{1}{2}})^2 &= 2/9
\end{aligned} \tag{14}$$

One advantage of the unitary approach for deriving CFP's is that the same techniques may be used for any shell. However, its utility is most convincing when dealing with more than half filled shells. Using the Gelfand basis, it is a simple matter to relate the CFP's for less than half shells ℓ^n to those CFP's for more than half filled shells ℓ^{n^*} where $n^* = 4\ell + 2 - n$. In the Racah basis this is a difficult task and various errors exist in the literature. A systematic derivation of the "particle" and "hole" CFP relations, referencing those errors, has recently been given by McQuire.¹⁵

In order to discuss more than half filled shells we first need to define the Gelfand state $|a^* \rangle$ associated with Gelfand state $|a \rangle$ of configuration ℓ^n . We show the associated Gelfand states diagrammatically in Figs. 2 and 3.⁶

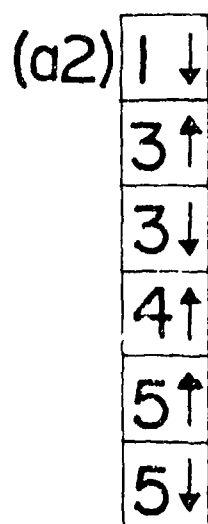
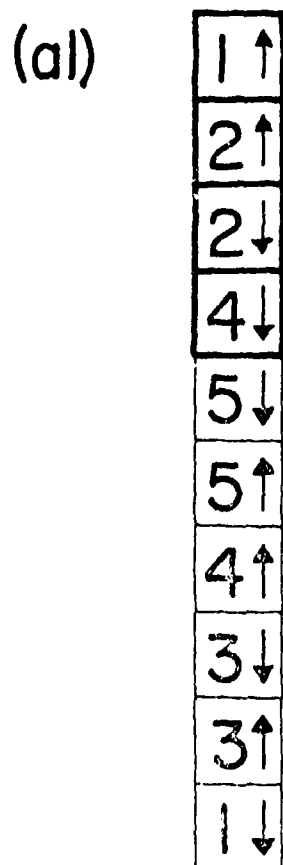
Using the associated Gelfand state leads to very simple relations between "particle" and "hole" states in the Gelfand basis. Indeed, it has been shown in Ref. 6 that

Fig.2. Associated Gelfand Basis



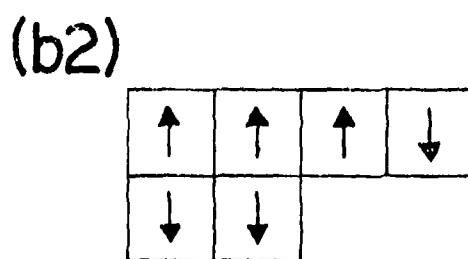
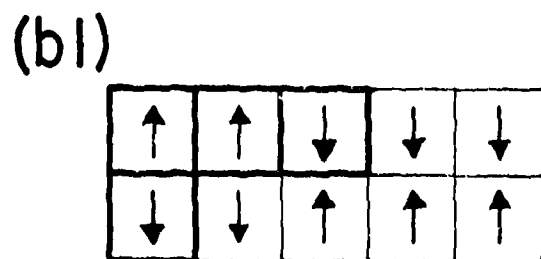
- a) $|a^*\rangle$ is found by completing a rectangle about $|a\rangle$ with 2 columns and $2l+1$ rows.
- b) The empty boxes are numbered increasing upward in the columns with no number in a column repeated.
- c) $|a\rangle$ is then detached from the rectangle and the remaining pattern rotated to give $|a^*\rangle$.

Fig. 3. Associated Basis for Antisymmetric and Spin States



a1) A rectangle is completed about the antisymmetric Gelfand state of $SU(4\lambda+2)$ with 1 column and $4\lambda+2$ rows. The empty boxes are numbered lexically as shown. Note that $n\uparrow > n\downarrow$.

a2) The state is then detached from the rectangle and the remaining pattern rotated to give the associated state.



b1) A rectangle is completed about the Gelfand state of $SU(2)$ with $2\lambda+1$ columns and 2 rows. The empty boxes are numbered lexically as shown. Note that $\uparrow > \downarrow$.

b2) The state is then detached from the rectangle and the remaining pattern rotated to give the associated state.

$$|(\ell^n {}_{LM_L})^*> = |\ell^{n^*} {}_{L-M_L}> \quad (15)$$

and

$$|(A_n \ell^n {}_{LM_L}, SM_S)^*> = (-1)^P |A_{n^*} \ell^{n^*} {}_{L-M_L}, S-M_S>, \quad (16)$$

where

$$P = n(\frac{n}{4} + S + \frac{1}{2}) - S^2 - M_L.$$

Now, from Eq. (16) and the simple relation¹⁶

$$\begin{aligned} & \langle A_{n-1} \ell^{n-1} {}_{\bar{L}M_L}, \bar{S}M_S; x\sigma | E_{xq} | A_n \ell^n {}_{LM_L}, SM_S \rangle \\ &= \langle (A_n \ell^n {}_{LM_L}, SM_S)^*; x\sigma | E_{xq} | (A_{n-1} \ell^{n-1} {}_{\bar{L}M_L}, \bar{S}M_S)^* \rangle (-1)^{\ell+q+\frac{1}{2}+\sigma}, \end{aligned} \quad (17)$$

we have

$$\begin{aligned} & \sqrt{n} C_{M_S 0 M_S}^{\bar{S} \frac{1}{2} S} C_{M_L q M_L}^{\bar{L} \ell L} (\ell^{n-1} {}_{\bar{L}S} |) \ell^n {}_{LS} \rangle \\ &= (-1)^{S+\bar{S}-\frac{1}{2}+\ell} \sqrt{\bar{n}} C_{-M_S \sigma -M_S}^{S \frac{1}{2} \bar{S}} C_{-M_L q -M_L}^{L \ell \bar{L}} (\ell^{\bar{n}-1} {}_{LS} |) \ell^{\bar{n}} {}_{\bar{L}S} \rangle (-1)^{\ell+q+\frac{1}{2}+\sigma}, \end{aligned} \quad (18)$$

where $\bar{n} = n^* + 1 = 4\ell+3 - n$.

Since

$$C_{m_1 m_2 m_3}^{j_1 j_2 j_3} = (-1)^{m_1 - m_3 - j_2} \sqrt{\frac{[j_3]}{[j_1]}} C_{-m_3 m_2 -m_1}^{j_3 j_2 j_1},$$

we have

$$(\ell^{n-1} {}_{\bar{L}S} |) \ell^n {}_{LS} \rangle = (-1)^{S+\bar{S}-\frac{1}{2}+\ell} \sqrt{\frac{[\bar{S}][\bar{L}]\bar{n}}{[S][L]n}} (\ell^{\bar{n}-1} {}_{LS} |) \ell^{\bar{n}} {}_{\bar{L}S} \rangle. \quad (19)$$

Our relation is in agreement with the Racah's except for a phase factor $(-1)^{L+\bar{L}}$. If we let the associated bases obey

$$|(\ell^n {}_{LM_L})^*> = (-1)^L |\ell^{n^*} {}_{L-M_L}>$$

instead of Eq. (15), we would agree with Racah's results. The choice of phase is arbitrary however; we prefer to use the simpler relation for associated bases.

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This relation also follows directly from Fig. 3a.